Journal of Analytical and Applied Pyrolysis 109 (2014) 168–175

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Leaching of heavy metals from fast pyrolysis residues produced from different particle sizes of sewage sludge

Hongmei Jin[a,b,c,*], Renato O. Arazo[b,d], Jun Gao[e], Sergio Capareda[b], Zhizhou Chang[a,c]

[a] Institute of Agricultural Resources and Environment, Jiangsu Academy of Agricultural Science, Jiangsu Agricultural Waste Treatment and Recycle Engineering Research Center, Nanjing 210014, PR China
[b] College of Biological and Agricultural Engineering, Texas A&M University, 77840, USA
[c] Key Laboratory of Agro-Environment in Downstream of Yangtze Plain, Ministry of Agriculture, Nanjing 210014, PR China
[d] Misamis Oriental State College of Agriculture and Technology, 9004, Philippines
[e] Nanjing Institute of Environmental Sciences, Ministry of Environmental Protection, Nanjing 210042, PR China

ARTICLE INFO

Article history:
Received 21 February 2014
Accepted 27 June 2014
Available online 5 July 2014

Keywords:
Fast pyrolysis residue
Sewage sludge
Particle size
Heavy metal
Leaching test

ABSTRACT

Pyrolysis residues produced from three particle sizes of sewage sludge using fluidized bed at 500 °C were subjected to toxicity characteristic leaching procedure (TCLP) and diethylenetriamine pentaacetic acid (DTPA) leaching tests to assess the potential release and bioavailability of heavy metals in their pyrolysis residues. Results showed that the smallest particle of sewage sludge produced the highest pyrolysis residue. Most functional characteristics of the pyrolysis residues were similar to those of sewage sludge itself, and some specific functional groups formed after fast pyrolysis. All heavy metals in feedstock sewage sludge were kept in pyrolysis residue except As, and their contents were enriched 2.5–3.5 times in pyrolysis residues. Pyrolysis residues obtained from larger particles of sewage sludge would cause excessive level of Cu and Zn. Although the fast pyrolysis significantly suppressed heavy metals leaching from residues, the leaching pattern of heavy metals was different between pyrolysis residues produced from the three particle sizes of sewage sludge. Specifically, Cu, Zn and As in the pyrolysis residues from the larger particle of sewage sludge were easier to be leached to environment. However, the bioavailability of Cu was highest in the pyrolysis residue derived from the largest particle of sewage sludge; whereas that of Zn and As was highest in the pyrolysis residue derived from the smallest particle of sewage sludge.

1. Introduction

Sewage sludge is a byproduct of the wastewater treatment process and is composed of organic compounds, macro and micronutrients, trace elements, microorganisms and micropollutants [1], which is identified as "a future waste problem" to resolve [2]. Specifically, in China more than 8 million tonnes (dry solid) of sewage sludge are produced annually, and the increase rate is very quick [3].

Pyrolysis can potentially be a method of choice for sewage sludge management [4], particularly compared to the current methods of landfilling and direct agricultural utilization [5]. Because this process can not only produce liquid fuel and chemicals [6], but also reduce the volume of the solid residue [7], eliminate pathogens [8], reduce some toxic compounds [9] in the original sewage sludge.

Fluidized bed pyrolysis, a kind of fast pyrolysis, is the most popular configuration due to its ease of operation and ready scale-up [4], and is being used on a commercial scale in many areas [10]. In a fluidized bed, particle size of the feedstock is one key factor that significantly influences the heat transfer process [11,12]. The choice of particle size coupled with appropriate feed rate could enhance good pyrolysis process by providing adequate supply of energy in the biomass particle size [4]. The particle size of feedstock influences the product yields and characteristics for reason that the feedstock residence time strongly depends on the particle size [4,13–16].

Solid residues are usually the main byproduct of sewage sludge pyrolysis for liquid and gas production, with the yield between 35 and 80 wt%, on a dry basis [17–19]. Application of pyrolysis residues produced from sewage sludge as amendments has potential to improve soil properties [20] and crop yield [21], decrease

* Corresponding author at: Institute of Agricultural Resources and Environment, Jiangsu Academy of Agricultural Sciences, Jiangsu Agricultural Waste Treatment and Recycle Engineering Research Center, Nanjing 210014, PR China.
Tel.: +86 025 84391252.
E-mail address: jinhm1201@hotmail.com (H. Jin).

http://dx.doi.org/10.1016/j.jaap.2014.06.016
0165-2370/

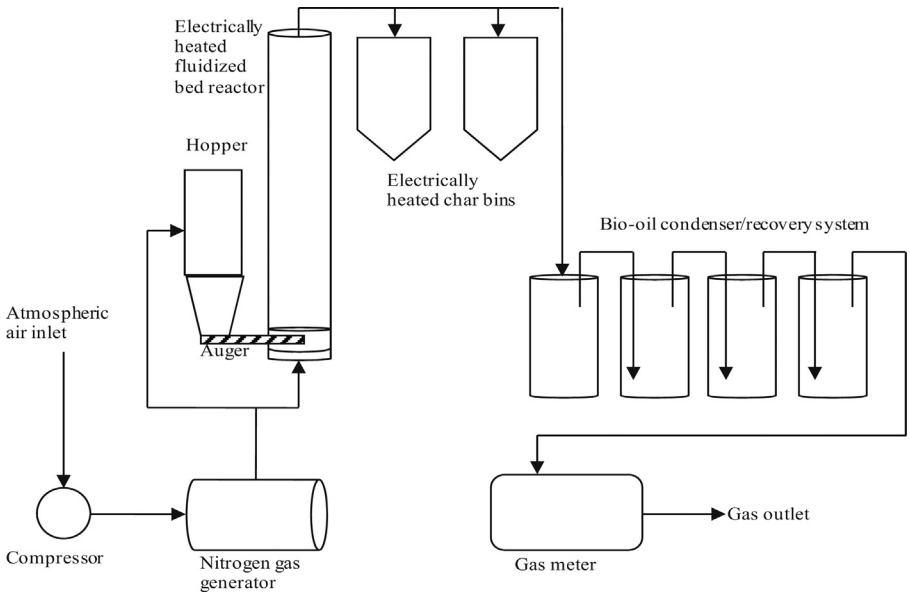

Fig. 1. Schematic diagram during fast pyrolysis of sewage sludge by fluidized bed unit.

the greenhouse gas emission [3], and for permanently sequester carbon [21,22]. But on the other hand, the majority of heavy metals originally contained in sewage sludge remain in its pyrolysis residues [18,22–25], except the volatile elements Hg and Cd [16,25]. Thus a risk assessment of potential soil and groundwater contamination should always be considered prior to the land application of pyrolysis residues produced from sewage sludge. The results from extraction and leaching experiments showed that heavy metals in sewage sludge-derived pyrolysis residues were significantly lower than those in sewage sludge itself [17,25]. The study from pot experiment also detected insignificant bioaccumulation of the trace metals present in the cherry tomato (*Lycopersicon esculentum*) fruits using wastewater sludge-derived pyrolysis residue [21].

Zhai et al. [16] employed three particle sizes of sewage sludge and three heating rates to study the pyrolysis process. They found that the mass loss was about 65 wt% of the total sludge mass at all experiment by means of the thermogravimetric analysis. However, less attention has been given to the effect of particle size on properties of the 35 wt% of pyrolysis residue, especially on its heavy metals. It is still unknown that whether the heavy metal contents in pyrolysis residue produced from different sewage sludge particles are distinct as well, and what is their potential environmental effects, which limit the reasonable treatment and land application security for sewage sludge-derived pyrolysis residues. Determining levels of heavy metals distributed in pyrolysis residues obtained from different particle size of sewage sludge and their forms by means of leaching test seems to offer valuable references for its risk assessment on environment and living organisms.

In this study, we mainly focused on Cu, Zn, Ni, Pb, Cd, Cr, and As in different particle sizes of sewage sludge and their fast pyrolysis residues as these heavy metals are common in sewage sludge, toxic to living organisms at high level and major metal pollutants in water bodies and soil environment around the world [26]. The specific objectives of this study were to: (1) determine the effect of particle size of sewage sludge on heavy metal distribution in its fast pyrolysis residues; (2) identify the potential leaching of heavy metals in pyrolysis residues produced from different particle size of sewage sludge; and (3) evaluate the feasibility of sewage sludge-derived pyrolysis residues for land application or reuse in view of the mobility and bioavailability of heavy metals.

2. Materials and methods

2.1. Fluidized bed pyrolysis

2.1.1. Feedstock preparation

The feedstock sewage sludge (SS) for the fast pyrolysis used in this study was obtained from the domestic waste after treatment at the Wastewater Treatment Plant, located in College Station, TX, USA. Then SS was activated and centrifuged for dewatering followed. Based on related work [16,27], some preparations were conducted before fast pyrolysis. First, SS was dried in an oven at 105 °C for 24 h. Then the dry SS was cracked from the original size (irregular clusters of the order of centimeters) into the size of around 1 mm using mallet. After that, the ground dry SS was shaken using Fisher Standard Brass Test Sieve (Fischer Scientific Company, MA, USA) to pass through 20 mesh (d = 0.830 mm) and 60 mesh (d = 0.180 mm). Therefore, three particle sizes of SS were obtained, i.e., >0.830 mm (SS1), 0.180–0.830 mm (SS2) and <0.180 mm (SS3). The samples were then kept in a desiccator for future use.

2.1.2. Fast pyrolysis experiment

The fast pyrolysis of SS1, SS2 and SS3 was conducted by the bench-scale fluidized bed setup in the Bio Energy Testing and Analysis (BETA) Laboratory of Texas A&M University (Fig. 1). The moisture content of the feedstock was ensured to be less than 10% prior to use to the pyrolysis process. Fluidization of SS was accomplished through the introduction of N_2 gas produced by the N_2 gas generator. The purpose of our whole project is to select the optimized fast pyrolysis conditions for bio-oil production using SS. The essential features of a fast pyrolysis process for producing liquids are moderate temperatures and short vapor residence time [28]. Usually, the reaction temperature is carefully controlled around 500 °C to maximize the liquid yield for most biomass, and vapor residence times of typically less than 2 s to minimize secondary reactions. According to the previous results in our lab, the reaction conditions in this study were selected in view of the optimized bio-oil yield, i.e., temperature of 500 °C and vapor residence time of 1.95 s. Pyrolysis residues of sewage sludge (SSC) were accumulated in the char bins of the unit, and collected after enough cooling in each running. Pyrolysis residues obtained from SS1, SS2

and SS3 were referred to as SSC1, SSC2 and SSC3. The samples were kept in a desiccator for appropriate analyses.

2.2. Leaching test

2.2.1. Chemical reagents

Deionized (DI) water was used to prepare all solutions throughout this study. Standard stock solutions were prepared from ultra-high purity grade chemicals or metals (99.99% pure or greater). All the chemicals used in the test were of analytical reagent grade conformed to the specifications of the Committee on Analytical Reagents of the American Chemical Society and purchased from VWR International, LLC.

2.2.2. Toxicity characteristic leaching procedure (TCLP)

In order to assess the potential leaching of heavy meta metals from different particle sizes of SS and their pyrolysis residues to environment, the TCLP test was applied. This method has been developed to simulate leaching of both organic and inorganic compounds and thus to determine the potential transfer of contaminants to a liquid medium. TCLP test applied in this study was modified from the Method 1311, US EPA [29]. The difference was that the sample weight was reduced from 100 g to 5 g.

Based on the TCLP method, two acetic acid extraction fluids of pH 4.93 ± 0.05 (No. 1) and 2.88 ± 0.05 (No. 2) were prepared, respectively. The first was used for the extraction of samples with pH less than 5.0, while the latter was applied to samples whose pH remained above 5.0, even after the addition of HCl. According to the procedure of TCLP method, pH was within the scope of 5.1–8.3 after adding 1 M HCl solution in SS and SSC slurries. Thus only extraction fluid No. 2 was used in the present experiment. After that, 5.0 g of each sample was placed in a vessel where the appropriate extraction liquid was added, with a liquid to solid ratio equal to 20. The extractor vessels were placed in a rotary agitation device and rotated for 18 ± 2 h at 30 ± 2 rpm in room temperature (25–30 °C). The tube was then shaken on a reciprocating shaker for 24 h and filtered through a 0.45-μm filtered membrane. Each treatment was two replication. Heavy metal concentrations in the filtrates were determined using inductively coupled plasma optical emission spectrometry (ICP-OES).

2.2.3. Diethylenetriamine pentaacetic acid (DTPA) leaching

The DTPA extractable fraction has been widely used to estimate bioavailability of heavy metals in soils and sludge [17,30], due to its capacity to chelate a wide range of metallic elements. Heavy metals in SS and SSC were DTPA extracted using the method of Lindsay and Norvell [31]. The heavy metals were extracted from 1.0 g of samples using 15 mL of a solution containing 5 mM DTPA and 10 mM $CaCl_2$ in a 50 mL polypropylene centrifuge tube. The tube was then shaken on a reciprocating shaker for 2 h, and filtered through a 0.45-μm filter membrane. The concentrations of DTPA-extractable heavy metals were then analyzed using ICP-OES.

2.3. Analysis and statistics

2.3.1. Basic characteristics

The moisture content of SS and SSC was determined by ASTM E1756. Proximate analysis of the samples was also done in accordance with ASTM standards (E1755 and D3172). The ultimate analysis was determined following ASTM D5373, with Vario MICRO Elemental Analyzer (Elementar Analysemsysteme GmbH, Germany). pH values were analyzed by the pH meter (Fisher Scientific Accumet, model 25 pH/ion meter, USA), with a liquid to solid ratio equal to 20.

2.3.2. Fourier transform infrared (FT-IR) analysis

FT-IR spectroscopy (Shimadzu, IR Affinity-1 with a MIRacle universal sampling accessory) was used to evaluate the structural properties of SS and SSC. The infrared spectra were collected in a range of 4000–600 cm^{-1} with resolution of 4 cm^{-1}. In order to minimize the sampling error, 10 subsamples were selected by random sampling from each sample of SS and SSC to measure FT-IR, and the average was used to analyze.

2.3.3. Heavy metal analysis

The total content of heavy metals in SS and SSC was determined by digesting samples in a mixture of HNO_3 and HCl (v/v was 3:1) according to SW-846 3052 method [32], and then analyzed according to SW-846 6010C method [33]. Briefly, the samples were dried and ground to pass through a USS #10 sieve. A representative sample of up to 0.5 g was digested in 9 mL of concentrated HNO_3 and 3 mL HCl for 15 min using a laboratory microwave heating system (reaching 180 ± 5 °C in approximately less than 5.5 min and remaining for 9.5 min). For each batch of samples processed, a method blank was carried throughout the entire sample preparation and analytical process. After cooling, the vessel contents were filtered and diluted to 100 mL with deionized water. Heavy metal concentrations in the dilution were determined using ICP-OES analytical technique (Spectro CirOS, Germany). In this study, the Zn, Cu, Cr, Ni, Pb, As and Cd contents of samples were determined. Meanwhile, analyses of standard reference materials (SRMs) containing known amounts of analytes in the media of interest were conducted for each batch of samples processed. Additional analyses were conducted whenever 80–120% accuracy of SRMs was not achievable.

2.3.4. Statistical method

One-way analysis of variance (ANOVA) was used for evaluating the effects of particle size on heavy metal contents in SS and SSC, respectively. Student's *t*-test was used for assessing the variations of heavy metal contents between SS and SSC. These statistical analyses were performed using procedures of SPSS (v. 13.0). Multiple means were compared with LSD test at $P = 0.05$.

3. Results and discussion

3.1. Characterization of SS and SSC

The total solids in SS1, SS2 and SS3 were reduced to 0.282, 0.297 and 0.403 kg/kg in the case of fluidized bed reactor at 500 °C, respectively. Different origins of the sewage sludge and its ash contents are the main reason for the final amount of residue after pyrolysis [4], and other factors, such as the temperature and the solid residence time, have also been identified as influential [34]. The largest particle of sewage sludge (SS1) produced less pyrolysis residue mainly on account of its lower ash content. However, SS2 produced less pyrolysis residue relative to SS3, although the ash content was significantly higher than that of SS3. This result implied that pyrolysis residue suppression did not only depend on the ash content; an increase in the solid residence time also causes a decrease in pyrolysis residue yields [15,35]. SS2 remained in the fluidized bed reactor for a longer time so that it can be completely burned before it was deposited in the char bins, and eventually resulted to less residue during fast pyrolysis. This was opposite with slow pyrolysis of SS with different particle sizes, which found SS with smaller particle size ($d < 0.25$ mm) obtained the largest total mass loss [16].

The different particle sizes of SS and residence time during fast pyrolysis might lead to the distinct characteristics of their residues. Results of pH, proximate analysis and ultimate analysis of SS and SSC were shown in Table 1. It demonstrated that pH in SSC was alkaline relative to that in SS, and the value was the highest in

Table 1
Basic characteristics in the three particle sizes of sewage sludge and their pyrolysis residues.

Indicators	SS1	SSC1		SS2	SSC2		SS3	SSC3	
pH	6.50 ± 0.10	7.60 ± 0.10	*	6.95 ± 0.05	9.10 ± 0.06	***	6.65 ± 0.05	7.85 ± 0.05	**
Proximate analysis (%)									
Moisture	5.9 ± 0.2	3.8 ± 0.3	*	5.2 ± 0.1	4.9 ± 0.1	ns	6.1 ± 0.1	3.0 ± 0.1	***
Volatile matter	69.3 ± 3.1	26.0 ± 3.6	**	55.7 ± 3.9	30.7 ± 4.4	*	70.9 ± 0.3	55.9 ± 3.2	*
Fixed C	11.1 ± 3.3	30.6 ± 7.9	*	12.4 ± 1.3	31.9 ± 2.0	**	4.9 ± 0.2	17.7 ± 2.7	**
Ash	13.6 ± 1.3	39.6 ± 4.5	ns	26.7 ± 5.0	32.5 ± 6.3	ns	18.2 ± 0.1	23.3 ± 0.5	*
Ultimate analysis (%)									
N	5.6 ± 1.5	5.3 ± 0.1	ns	4.4 ± 2.0	5.0 ± 0.9	ns	7.0 ± 0.1	6.6 ± 0.1	ns
C	31.1 ± 6.9	24.3 ± 0.8	ns	34.6 ± 6.1	30.7 ± 2.9	ns	37.1 ± 0.4	35.4 ± 0.4	ns
H	4.41 ± 1.02	1.30 ± 0.05	ns	4.74 ± 1.13	3.29 ± 0.59	ns	5.31 ± 0.02	4.89 ± 1.79	ns
S	0.47 ± 0.07	0.19 ± 0.07	ns	0.30 ± 0.05	0.22 ± 0.02	ns	0.36 ± 0.01	0.42 ± 0.10	ns
O[a]	44.8 ± 9.3	22.6 ± 0.8	ns	29.3 ± 6.8	28.3 ± 7.4	ns	32.1 ± 0.4	13.4 ± 2.3	ns

SS1, SS2 and SS3 indicated the feedstock sewage sludge with particle size $d > 0.830$ mm, d 0.180–0.830 mm and $d < 0.180$ mm, respectively; SSC1, SSC2 and SSC3 indicated the fast pyrolysis residues of SS1, SS2 and SS3, respectively.
Mean ± standard error of mean ($n = 3$).
ns, *, ** and *** indicated no statistical significance and significant differences between sewage sludge and its pyrolysis residues at levels of 0.05, 0.01 and 0.001, respectively.
[a] Calculated by difference.

SSC2. SSC contained significantly lower moisture and volatile matter, but higher fixed C and ash. The element contents indicated no significant differences between SS and SSC.

IR spectra of SS and SSC in near IR region (i.e., wavenumber: 3500–600 cm^{-1}) were demonstrated in Fig. 2. Briefly, the organic compounds in SS included carboxylic acids (1320–1000 cm^{-1}, 1695–1395 cm^{-1} and 3400–2500 cm^{-1}) [36,37], amides/amines (900–660 cm^{-1}, 1250–1000 cm^{-1}, 1650–1550 cm^{-1} and 3400–3100 cm^{-1}) [36,37], alcohols and phenols (1200–1000 and 3400–3100 cm^{-1}) [36–38], alkenes (730–675 cm^{-1} and 2250–2100 cm^{-1}), arenes (900–690 cm^{-1}), and isocyanates, isothiocyanates, diimides, azides and ketenes (2270–2100 cm^{-1}) [36–38], etc. The band at 2360 cm^{-1} was unique in SS1 and might be the P–H phosphine (2440–2280 cm^{-1}) [39]. The inorganic compounds mainly covered alumina-silicates (3500–3300 cm^{-1}, 1650–1600 cm^{-1} and 1100–1000 cm^{-1}), carbonates (1430 cm^{-1}), such as $CaCO_3$ (875–715 cm^{-1}) [40]. After fast pyrolysis at 500 °C, the spectrum of SSC demonstrated that most functional characteristics were similar to those of SS itself. Meanwhile some specific functional groups formed. For example, the spectrum of SSC1 showed a number of small absorption peaks in the region from 1900 to 1300 cm^{-1}, which might indicate the presence of inorganic compounds such as alumina-silicates, carbonates, metal oxides and sulfides, amongst others [40]. A absorption peak near 2043 cm^{-1} of SSC2 might be silicon functions.

3.2. Total contents of heavy metals in SS and SSC

Total heavy metal contents in different particle size of SS were shown in Table 2. Measurement results showed that the total heavy metal contents in SS varied greatly, which were in the order of Zn > Cu > Cr > Ni > Pb > As > Cd. This variation tendency was similar to the results reported by other studies [22,41,42]. Due to the domestic origin of the feedstock, the total contents of heavy metals

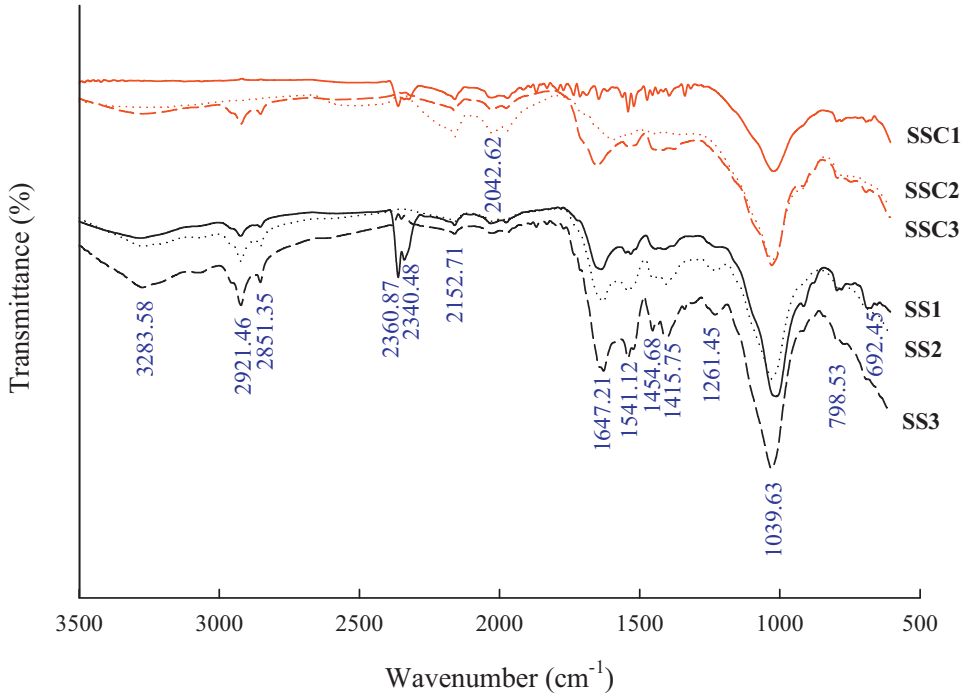

Fig. 2. FT-IR of the three particle sizes of sewage sludge and their pyrolysis residues. SS1, SS2 and SS3 indicated the feedstock sewage sludge with particle size $d > 0.830$ mm, d 0.180–0.830 mm and $d < 0.180$ mm, respectively; SSC1, SSC2 and SSC3 indicated the pyrolysis residues of SS1, SS2 and SS3, respectively.

Table 2
Measured and estimated heavy metal contents in the three particle sizes of sewage sludge.

Metals	SS1		SS2		SS3	
	Measured	Estimated[a]	Measured	Estimated[a]	Measured	Estimated[a]
Zn	559 ± 20	544 ± 23	453 ± 19	444 ± 18	432 ± 25	442 ± 2
Cu	224 ± 17	237 ± 8	139 ± 48	125 ± 14	183 ± 7	178 ± 5
Cr	16.1 ± 1.2	15.6 ± 1.1	19.7 ± 2.2	19.3 ± 3.2	24.7 ± 2.6	24.9 ± 0.4
Ni	14.3 ± 1.1	14.7 ± 0.4	14.0 ± 0.7	14.3 ± 0.8	20.7 ± 2.1	20.1 ± 2.0
Pb	23.3 ± 5.6	22.3 ± 2.9	17.1 ± 0.5	18.1 ± 0.9	25.5 ± 0.4	26.3 ± 3.4
As	18.5 ± 0.8	12.4 ± 1.3	18.7 ± 0.3	15.1 ± 2.3	26.9 ± 0.4	18.8 ± 1.6
Cd	1.85 ± 0.09	1.66 ± 0.01	1.87 ± 0.03	1.76 ± 0.25	1.80 ± 0.03	1.68 ± 0.17

SS1, SS2 and SS3 indicated the feedstock sewage sludge with particle size $d > 0.830$ mm, d 0.180–0.830 mm and $d < 0.180$ mm, respectively; unit: mg/kg dry weight.
Mean ± standard error of mean ($n = 2$).
[a] Values were calculated as follows: C_e (mg/kg dry weight) = $C_i \times R_i$, where C is metal content of SSC, R is the yield rate of SSC, i is the particle size, and $R_1 = 28.2\%$, $R_2 = 29.7\%$, $R_3 = 40.3\%$.

in the current study were lower than other reports [17,22,41] and below the permitted value, which restricted its land application [43–45].

In order to understand the heavy metal balances before and after fast pyrolysis, the heavy metal contents of SS were estimated from those of SSC. Data in Table 2 showed that few heavy metals in SS lost through volatilization during the fast pyrolysis at 500 °C except for As, implying that most heavy metals were kept in SSC. The yield rates of SSC were 28.2%, 29.7% and 40.3%, respectively, produced from the three particle sizes of SS. On the basis of these yield rates, the content of heavy metals were proximately enriched 3.5, 3.4 and 2.5 times, respectively, in SSC1, SSC2 and SSC3. It was worth noting that the loss rate of As ranged from 19.3% to 32.6%. Yan et al. (2008) reported that 62.5% of the total emitted As was volatilized below 400 °C and the reduction of As(V) to As(III) is responsible for As volatilization during incineration of hyper-accumulators at this temperature. Therefore, there would be high risk of As volatilization from SS using fast pyrolysis at 500 °C.

3.3. Heavy metal distribution in different particle sizes of SS and SSC

The distribution pattern of heavy metals among the three particle sizes of SS and SSC were shown in Fig. 3. The data indicated that fluidized bed pyrolysis used in this study presented the advantages of concentrating on the heavy metals in the three particle sizes of SSC as a result of organic matter decomposition and decrease in volume of SS [21,22,41]. This finding was similar with other studies [17,22,41,46] and also supported the estimated results in Table 2. However, even these heavy metals measured in the three particle sizes of SSC were below the permitted land application values in US EPA standards [43] and European Union Council Directive 86/278/EEC [44].

Zn and Cu were relatively higher in the largest particles of sewage sludge (SS1), in which Zn content was significantly ($P \leq 0.05$) higher than those in smaller particles (SS2 and SS3) (Fig. 3a and b). In contrast, Cr, Ni, Pb and As were higher in the smallest particles (SS3), in which the contents of Ni and As were significantly ($P \leq 0.05$) higher than those in larger particles (SS1 and SS2) (Fig. 3d and f). Cd content in SS distributed evenly between those three particle sizes (Fig. 3g).

When it came to the pyrolysis residues, the contents of Cu (839 mg/kg dry weight) and Zn (1928 mg/kg dry weight) in SSC1 surpassed or approached the permitted values in China (800 and 2000 mg/kg dry weight, respectively) if it was to be applied to soil with a pH < 6.5 [45]. This finding is of great importance, in terms of agricultural applications, since pyrolysis residues obtained from larger particles of sewage sludge would cause excessive level of specific heavy metals.

3.4. Leaching of heavy metals from different particle size of SS and SSC

The leaching test plays a vital role in assessing the environmental impact of disposal [25]. The leaching contents of heavy metals in SS were presented in Table 3. The maximum TCLP-leaching contents of heavy metals happened to SS1 for Cu, SS2 for Zn, Ni and Cd, and SS3 for As, respectively; while those happened to SS1 for Zn, Cu, Cr and Ni, SS2 for As and Cd, and SS3 for Pb, respectively, based on DTPA-leaching method. It indicated that the potential transfer of

Table 3
Leaching content of heavy metals from the three particle sizes of pyrolysis residues produced from sewage sludge.

	Zn	Cu	Cr	Ni	Pb	As	Cd
TCLP leaching							
SS1	6.16 ± 0.60	6.80 ± 1.76	<0.40	1.57 ± 0.31	<0.40	0.48 ± 0.00	<0.40
SSC1	<0.40	<1.00	<0.40	<0.40	<0.40	0.44 ± 0.01	<0.40
SS2	6.84 ± 0.42	4.82 ± 0.58	<0.40	1.40 ± 0.30	<0.40	0.52 ± 0.02	0.48 ± 0.06
SSC2	<0.40	<1.00	<0.40	<0.40	<0.40	0.47 ± 0.01	<0.40
SS3	3.41 ± 0.81	4.01 ± 0.79	<0.40	1.55 ± 0.15	<0.40	0.58 ± 0.02	<0.40
SSC3	1.43 ± 0.05	1.82 ± 0.04	<0.40	<0.40	<0.40	0.44 ± 0.06	<0.40
DTPA leaching							
SS1	11.94 ± 1.18	25.86 ± 1.06	3.25 ± 0.25	2.05 ± 0.14	1.66 ± 0.16	1.28 ± 0.13	0.49 ± 0.01
SSC1	3.50 ± 0.09	8.86 ± 2.35	2.71 ± 0.32	1.44 ± 0.21	1.02 ± 0.06	0.81 ± 0.07	0.45 ± 0.03
SS2	6.42 ± 0.66	22.44 ± 2.68	2.62 ± 0.06	1.43 ± 0.32	1.74 ± 0.21	2.00 ± 0.14	0.70 ± 0.10
SSC2	1.53 ± 0.11	2.27 ± 0.29	1.15 ± 0.15	1.20 ± 0.24	1.15 ± 0.25	0.98 ± 0.02	0.45 ± 0.18
SS3	9.04 ± 0.48	6.13 ± 0.16	1.54 ± 0.54	1.98 ± 0.36	2.28 ± 0.81	1.96 ± 0.49	0.52 ± 0.03
SSC3	6.40 ± 0.08	5.90 ± 0.18	0.46 ± 0.02	0.89 ± 0.11	1.27 ± 0.27	1.44 ± 0.44	0.42 ± 0.08

SS1, SS2 and SS3 indicated the feedstock sewage sludge with particle size $d > 0.830$ mm, d 0.180–0.830 mm and $d < 0.180$ mm, respectively; SSC1, SSC2 and SSC3 indicated the pyrolysis residues of SS1, SS2 and SS3, respectively.
Unit: mg/kg dry weight.
Mean ± standard error of mean ($n = 2$).

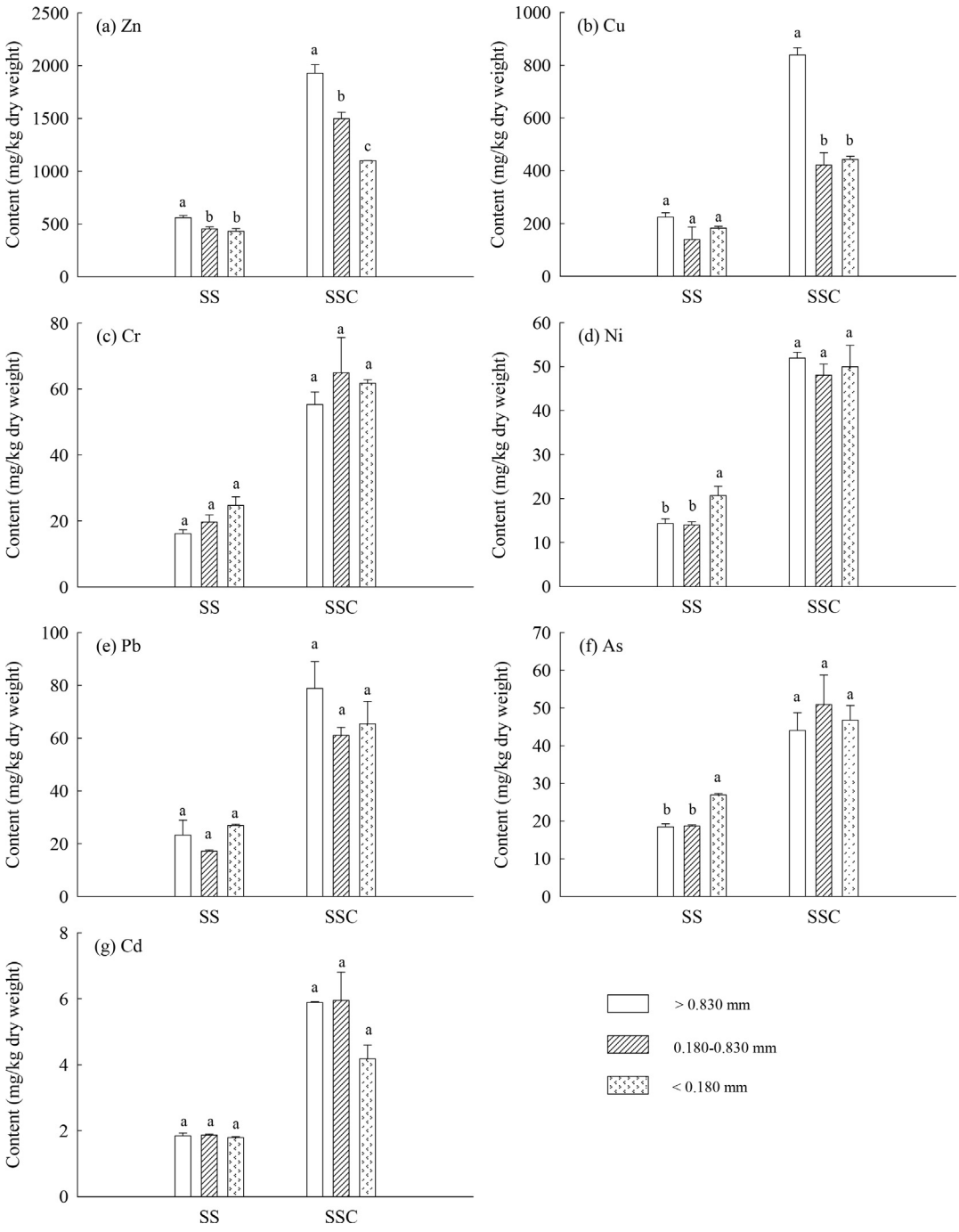

Fig. 3. Total content of heavy metals in the three particle sizes of sewage sludge and their pyrolysis residues. Mean ± standard error of mean ($n = 2$); different letters indicate significant ($P \leq 0.05$) differences between the three particle sizes (i.e., $d > 0.830$ mm, d 0.180–0.830 mm, and $d < 0.180$ mm); SS, feedstock sewage sludge; SSC, sewage sludge-derived pyrolysis residue.

heavy metals to a liquid medium (TCLP-leaching) could not always reflect their bioavailability (DTPA-leaching) in different particle size of SS. Generally, the TCLP-leaching contents of heavy metals in SS were less than 4% of the total heavy metal contents, and only in the case of Ni it reached 11.2% (Fig. 4); whereas DTPA method exhibited better performance in heavy metal leaching compared to TCLP method (Fig. 5).

The fast pyrolysis significantly suppressed heavy metals leaching from the residues: TCLP-leaching and DTPA-leaching contents of heavy metals from SSC were lower than 2.0 and 9.0 mg/kg dry weight, respectively (Table 3). The percentage of the TCLP-leaching heavy metals from SSC was very low (<0.9%) except for As (approximately 1.02% in SSC1, 0.94% in SSC2, and 0.93% in SSC3), which was significantly ($P \leq 0.05$) higher than those in SS (Fig. 4). Using DTPA-leaching method, the percentage of heavy metal contents in leachates of SSC were in the range of 0.1–0.6%, 0.6–1.3%, 0.8–4.9%, 1.8–2.8%, 1.3–2.0%, 1.8–3.2%, and 7.3–9.9% of the total contents of Zn, Cu, Cr, Ni, Pb, As and Cd, respectively, which were significantly ($P \leq 0.05$ or 0.01) lower than those in SS except for Cr, Pb and As in SSC3 (Fig. 5c). The leaching contents of Cr (0.023–0.163 mg/L), Cd (0.021–0.035 mg/L), Pb (0.051–0.115 mg/L), and As (0.041–0.100 mg/L) were rather low and meet the maximum content of contaminants for the toxicity characteristic (i.e., Cr 5.0 mg/L, Cd 1.0 mg/L, Pb, 5.0 mg/L, and As 5.0 mg/L) [43].

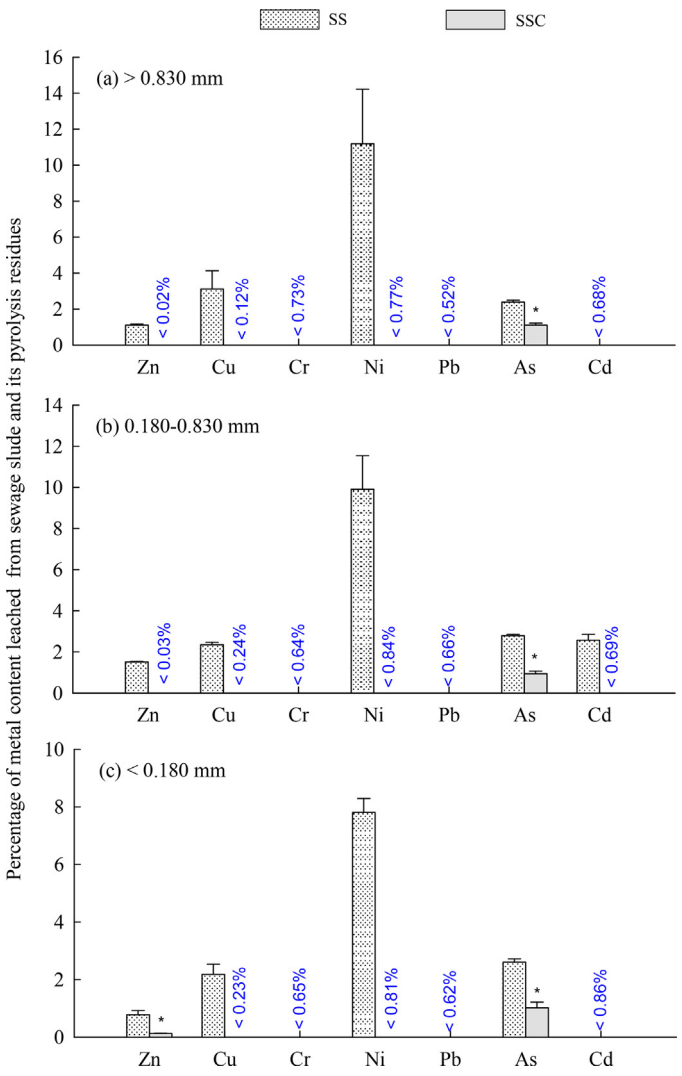

Fig. 4. Percentage of heavy metal contents leached from the three particle sizes of sewage sludge and their pyrolysis residues based on TCLP method. Mean ± standard error of mean ($n = 2$); * indicated no statistical significance and significant differences between sewage sludge and its pyrolysis residues at levels of 0.05; absent bars indicated that the data were particularly low and were shown by number; SS, feedstock sewage sludge; SSC, sewage sludge-derived pyrolysis residue.

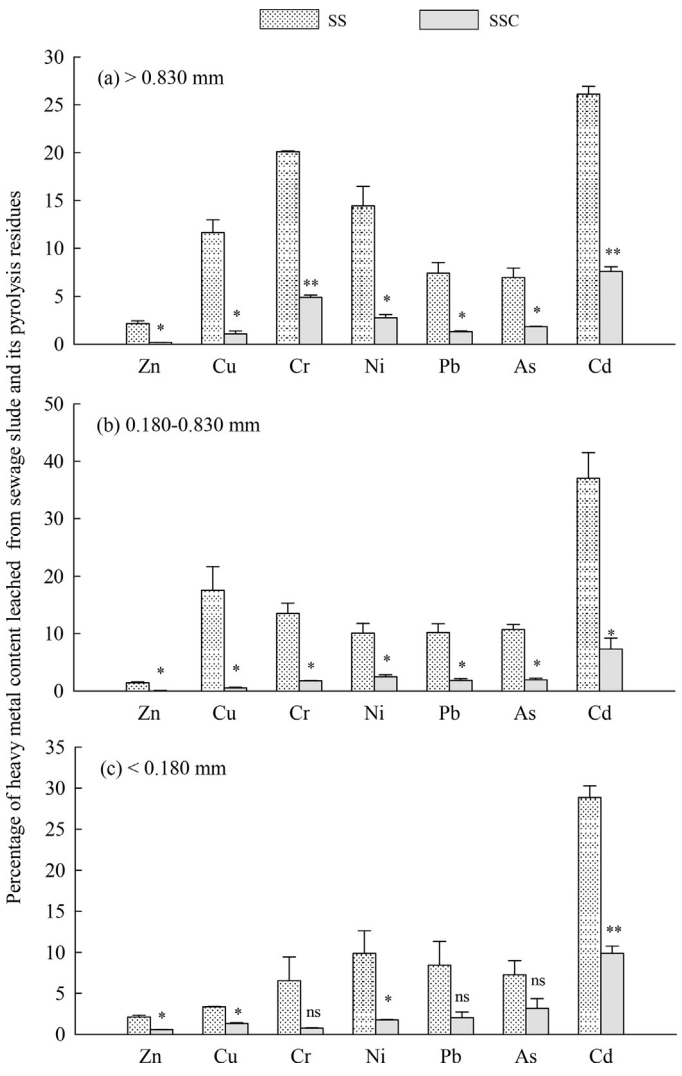

Fig. 5. Percentage of heavy metal contents leached from the three particle sizes of sewage sludge and their pyrolysis residues based on DTPA method. Mean ± standard error of mean ($n = 2$); ns, * and ** indicated no statistical significance and significant differences between sewage sludge and its pyrolysis residues at levels of 0.05 and 0.01, respectively; SS, feedstock sewage sludge; SSC, sewage sludge-derived pyrolysis residue.

Leaching patterns of heavy metals in the three particle sizes of SS were also changed after fast pyrolysis (Table 3). Mizutani et al. [47] found that particle size preparation can influence heavy metal leaching behavior from municipal solid wastes, and larger surface areas per mass or volume can allow more rapid dissolution at the surface. In this study, TCLP-leaching contents of Zn and Cu and DTPA-leaching content of Zn, Pb and As were highest in SSC3, which would be ascribed to the larger surface area of SSC3. In contrast, other heavy metal contents, like TCLP-leaching Pb, Cd, Cr, Ni and DTPA-leaching Cu, Cr and Cd were highest in SSC1, indicating that other characteristics of pyrolysis residues play important roles on heavy metal leaching as well.

On the one hand, materials with a high pH value tend to restrain heavy metal release [48]. The higher alkaline pH of the SSC2 (i.e., 9.10) could explain that lower leaching contents of most heavy metals were found in this study. On the other hand, the contents of As and Ni leached from SSC2 were higher than those from SSC1 and SSC3, implying that specific metal leaching suppression did not only depend on the pH of the samples. It has been reported that compounds and functional groups of pyrolysis residue might enhance its ability to immobilize heavy metals [17,22,41]. Previous FT-IR analyses in this study had revealed the presence of a great number of organic and inorganic compounds and some differences of functional groups between SSC1, SSC2 and SSC3 (Fig. 2). The nitrogen-containing groups (i.e., amine and amides) preserved after fast pyrolysis may serve as ligands for binding metals in the feedstock and combining into the residue of carbon structure network; while the abundant functional groups (such as carboxyl and hydroxyl) may contribute to the formation of organometallic complex in the pyrolysis residue particles.

Although results from leaching tests provided transfer trends of heavy metals in different particles sizes of SSC, further research is needed in order to examine whether the heavy metals are plant available or not as plant-heavy metal availability is affected by both soil processes and plant factors.

4. Conclusion

During the fluidized bed pyrolysis at 500 °C, particle sizes of sludge sewage can significantly influence the distribution of total heavy metals and their leaching characteristics in pyrolysis residues. All heavy metals in feedstock sewage sludge were kept

in pyrolysis residue except As, and their contents were enriched 3.5, 3.4 and 2.5 times, respectively, in SSC1, SSC2 and SSC3. Among all of the measured heavy metals, high contents of Cu and Zn were found in pyrolysis residues obtained from larger particles of sewage sludge, putting them at higher risk of surpassing the permitted land application values, especially to soil with a pH < 6.5. The variations of surface area, pH, compounds and functional groups among SSC1, SSC2 and SSC3 could induce distinct heavy metal leaching difference. On the whole, TCLP-leaching and DTPA-leaching contents of heavy metals from SSC were lower than 2.0 and 9.0 mg/kg dry weight, respectively, which were less than 1% and 10% of the total content of heavy metals, and meet the maximum content of contaminants for the toxicity characteristic. Specifically, Cu, Zn and As in the pyrolysis residues from the larger particle of sewage sludge were easier to be leached to environment. However, further research is needed to examine the bioavailability of these metals as plant-heavy metal availability is affected by both soil processes and plant factors. The findings in this study are especially very important to have a better understanding of the particle size preparation of feedstock using fluidized bed pyrolysis, and the mobility and bioavailability of the heavy metals present in their pyrolysis residues, before field trials are attempted.

Acknowledgements

This study was funded by the National Natural Science Foundation of China (No. 21107038), the Independent Innovation Fund of Agricultural Science and Technology of Jiangsu Province (No. CX(12)5055), the Special Fund for Agro-scientific Research in the Public Interest (No. 201203050), and Natural Science Foundation of Jiangsu Province (No. 2011079). We also wish to thank Dr. Jersson Plácido and Dr. Robert J. Taylor for their kind cooperation in measurement and sample determination in Texas A&M University.

References

[1] Y. Tian, J. Zhang, W. Zuo, L. Chen, Y. Cui, T. Tan, Nitrogen conversion in relation to NH_3 and HCN during microwave pyrolysis of sewage sludge, Environ. Sci. Technol. 47 (2013) 3498–3505.
[2] R. Han, J. Liu, Y. Zhang, X. Fan, W. Lu, H. Wang, Dewatering and granulation of sewage sludge by biophysical drying and thermo-degradation performance of prepared sludge particles during succedent fast pyrolysis, Bioresour. Technol. 107 (2012) 429–436.
[3] Y. Cao, A. Pawłowski, Sewage sludge-to-energy approaches based on anaerobic digestion and pyrolysis: brief overview and energy efficiency assessment, Renew. Sustain. Energy Rev. 16 (2012) 1657–1665.
[4] I. Fonts, G. Gea, M. Azuara, J. Ábrego, J. Arauzo, Sewage sludge pyrolysis for liquid production: a review, Renew. Sustain. Energy Rev. 16 (2012) 2781–2805.
[5] Y. Kim, W. Parker, A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil, Bioresour. Technol. 99 (2008) 1409–1416.
[6] T. Karayildirim, J. Yanik, M. Yuksel, H. Bockhorn, Characterisation of products from pyrolysis of waste sludges, Fuel 85 (2006) 1498–1508.
[7] Y. Yuan, T. Yuan, D. Wang, J. Tang, S. Zhou, Sewage sludge biochar as an efficient catalyst for oxygen reduction reaction in an microbial fuel cell, Bioresour. Technol. 144 (2013) 115–120.
[8] R. Maureen, The case against land application of sewage sludge pathogens, Can. J. Infect. Dis. 12 (2001) 205–207.
[9] Z.R. Xu, W. Zhu, M. Li, H.W. Zhang, M. Gong, Quantitative analysis of polycyclic aromatic hydrocarbons in solid residues from supercritical water gasification of wet sewage sludge, Appl. Energ. 102 (2013) 476–483.
[10] C. Briens, J. Piskorz, F. Berruti, Biomass valorization for fuel and chemicals production – a review, Int. J. Chem. React. Eng. 6 (2008) 1–49.
[11] T.A. Ngo, J. Kim, S.S. Kim, Fast pyrolysis of palm kernel cake using a fluidized bed reactor: design of experiment and characteristics of bio-oil, J. Ind. Eng. Chem. 19 (2013) 137–143.
[12] M.R. Stammbach, B. Kraaz, R. Hagenbucher, W. Richarz, Pyrolysis of sewage sludge in a fluidized bed, Energy Fuels 3 (1989) 255–259.
[13] S. Septien, S. Valin, C. Dupont, M. Peyrot, S. Salvador, Effect of particle size and temperature on woody biomass fast pyrolysis at high temperature (1000–1400 °C), Fuel 97 (2012) 202–210.
[14] H.J. Park, H.S. Heo, Y.-K. Park, J.-H. Yim, J.-K. Jeon, J. Park, C. Ryu, S.-S. Kim, Clean bio-oil production from fast pyrolysis of sewage sludge: effects of reaction conditions and metal oxide catalysts, Bioresour. Technol. 101 (2010) S83–S85.
[15] I. Fonts, A. Juan, G. Gea, M.B. Murillo, J.L. Sánchez, Sewage sludge pyrolysis in fluidized bed, 1: influence of operational conditions on the product distribution, Ind. Eng. Chem. Res. 47 (2008) 5376–5385.
[16] Y. Zhai, W. Peng, G. Zeng, Z. Fu, Y. Lan, H. Chen, C. Wang, X. Fan, Pyrolysis characteristics and kinetics of sewage sludge for different sizes and heating rates, J. Therm. Anal. Calorim. 107 (2012) 1015–1022.
[17] H. Lu, W. Zhang, S. Wang, L. Zhuang, Y. Yang, R. Qiu, Characterization of sewage sludge-derived biochars from different feedstocks and pyrolysis temperatures, J. Anal. Appl. Pyrolysis 102 (2013) 137–143.
[18] Y. Chun, D. Ji, K. Yoshikawa, Pyrolysis and gasification characterization of sewage sludge for high quality gas and char production, J. Mech. Sci. Technol. 27 (2013) 263–272.
[19] I. Fonts, M. Azuara, G. Gea, M.B. Murillo, Study of the pyrolysis liquids obtained from different sewage sludge, J. Anal. Appl. Pyrolysis 85 (2009) 184–191.
[20] G. Gascó, J. Paz-Ferreiro, A. Méndez, Thermal analysis of soil amended with sewage sludge and biochar from sewage sludge pyrolysis, J. Therm. Anal. Calorim. 108 (2012) 769–775.
[21] M.K. Hossain, V. Strezov, K. Yin Chan, P.F. Nelson, Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (*Lycopersicon esculentum*), Chemosphere 78 (2010) 1167–1171.
[22] I.H. Hwang, Y. Ouchi, T. Matsuto, Characteristics of leachate from pyrolysis residue of sewage sludge, Chemosphere 68 (2007) 1913–1919.
[23] I. Velghe, R. Carleer, J. Yperman, S. Schreurs, Study of the pyrolysis of sludge and sludge/disposal filter cake mix for the production of value added products, Bioresour. Technol. 134 (2013) 1–9.
[24] M.K. Hossain, V. Strezov, K.Y. Chan, A. Ziolkowski, P.F. Nelson, Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar, J. Environ. Manage. 92 (2011) 223–228.
[25] A.B. Hernandez, J.H. Ferrasse, P. Chaurand, H. Saveyn, D. Borschneck, N. Roche, Mineralogy and leachability of gasified sewage sludge solid residues, J. Hazard. Mater. 191 (2011) 219–227.
[26] WHO, Guidelines for drinking-water quality, in: Chemical Fact Sheets, World Health Organization, Geneva, 2004.
[27] X. Yuan, H. Huang, G. Zeng, H. Li, J. Wang, C. Zhou, H. Zhu, X. Pei, Z. Liu, Z. Liu, Total concentrations and chemical speciation of heavy metals in liquefaction residues of sewage sludge, Bioresour. Technol. 102 (2011) 4104–4110.
[28] A.A. Khan, W. de Jong, P.J. Jansens, H. Spliethoff, Biomass combustion in fluidized bed boilers: potential problems and remedies, Fuel Process. Technol. 90 (2009) 21–50.
[29] US EPA, Method 1311, Toxicity Characteristic Leaching Procedure (TCLP), US EPA, Washington, DC, 1992.
[30] P.K.A. Hong, C. Li, S.K. Banerji, Y. Wang, Feasibility of metal recovery from soil using DTPA and its biostability, J. Hazard. Mater. 94 (2002) 253–272.
[31] W.L. Lindsay, W.A. Norvell, Development of a DTPA soil test for zinc, iron, manganese, and copper, Soil Sci. Soc. Am. J. 42 (1978) 421–428.
[32] US EPA, SW-846, Method 3052, Acid Digestion of Sediments, Sludges, and Soils, US EPA, 1996.
[33] US EPA, SW-846, Method 6010C, Inductively Coupled Plasma-Atomic Emission Spectrometry, US EPA 6010, 2007.
[34] C. Jindarom, V. Meeyoo, B. Kitiyanan, T. Rirksomboon, P. Rangsunvigit, Surface characterization and dye adsorptive capacities of char obtained from pyrolysis/gasification of sewage sludge, Chem. Eng. J. 133 (2007) 239–246.
[35] L. Shen, D.K. Zhang, An experimental study of oil recovery from sewage sludge by low-temperature pyrolysis in a fluidised-bed, Fuel 82 (2003) 465–472.
[36] Y. Chen, L. Guo, H. Jin, J. Yin, Y. Lu, X. Zhang, An experimental investigation of sewage sludge gasification in near and super-critical water using a batch reactor, Int. J. Hydrogen Energy 38 (2013) 12912–12920.
[37] J. Ábrego, J. Arauzo, J.L. Sánchez, A. Gonzalo, T. Cordero, J. Rodríguez-Mirasol, Structural changes of sewage sludge char during fixed-bed pyrolysis, Ind. Eng. Chem. Res. 48 (2009) 3211–3221.
[38] H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, Fuel 86 (2007) 1781–1788.
[39] J. Coates, Interpretation of infrared spectra, a practical approach, Encyclopedia Anal. Chem. (2000) 1–24.
[40] N. Said, S.A. El-Shatoury, L.F. Díaz, M. Zamorano, Quantitative appraisal of biomass resources and their energy potential in Egypt, Renew. Sustain. Energy Rev. 24 (2013) 84–91.
[41] Y.D. He, Y.B. Zhai, C.T. Li, F. Yang, L. Chen, X.P. Fan, W.F. Peng, Z.M. Fu, The fate of Cu, Zn, Pb and Cd during the pyrolysis of sewage sludge at different temperatures, Environ. Technol. 31 (2010) 567–574.
[42] T.B. Chen, Q.F. Huang, D. Gao, Y.Q. Zheng, J.-F. Wu, Heavy metal concentrations and their decreasing trends in sewage sludges of China, Acta Sci. Circumst. 23 (2003) 561–569.
[43] US EPA, Code of Federal Regulations, 40CFR Chapter I 261.24 Toxicity characteristic, 2013.
[44] 86/278/EEC, Sewage Sludge Directive 86/278/EEC, 1986.
[45] GB 18918-2002, Discharge standard of pollutants for municipal wastewater treatment plant, 2002.
[46] W. Kaminsky, A.B. Kummer, Fluidized bed pyrolysis of digested sewage sludge, J. Anal. Appl. Pyrolysis 16 (1989) 27–35.
[47] S. Mizutani, N. Watanabe, S. Sakai, H. Takatsuki, Influence of particle size preparation of MSW incineration residues on heavy metal leaching behavior in leaching tests, Environ. Sci. 13 (2006) 363–370.
[48] R.C. Kistler, F. Widmer, P.H. Brunner, Behavior of chromium, nickel, copper, zinc, cadmium, mercury, and lead during the pyrolysis of sewage sludge, Environ. Sci. Technol. 21 (1987) 704–708.